Rheological investigations of a polymeric precursor for ceramic materials: experiments and theoretical modeling

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The paper is concerned with the rheological investigation of a commercial polysiloxane of the form $[CH_3\text{-}SiO_{3/2}]_x$ which has potential application as precursor for the synthesis of silicon oxycarbide ceramics. The cross-linking reaction of pre-ceramic polymers in the presence of catalyst and/or fillers is one of the key steps in the successful polymer-to-ceramic transformation process. During the proceeding cross-linking reaction, a fast change of the polymer rheology is observed. The route of time-temperature variation for elasticity and viscosity of the samples is of great importance for the final properties of the resulting ceramic material. Dynamic test at constant oscillatory frequency and different constant temperatures or temperature gradients have been performed in order to establish the time evolution of the elastic and viscous moduli, as a function of the catalyst and filler concentration. The experimental data are modelled with a novel constitutive relation which is able to reproduce the rheology of isothermal and non-isothermal cross-linking processes as a function of the reaction time. The qualitative agreement between experiments and numerical simulations of the process is obtained for all the tests. The results of the present study indicate the value of rheological measurements to determine the thermomechanical properties of pre-ceramic polymers.

1. Introduction

Polymer derived Si-based ceramics are materials under development in a wide range of novel applications such as: protective coatings, porous materials, ceramic matrix composites for high temperature and/or for electronic packaging. Recently, polysiloxanes have been used as precursors for the synthesis of silicon oxycarbide ceramics. Pyrolysis of various pre-ceramic polysiloxanes under argon or ammonia offers a possibility to prepare silicon oxycarbide or oxynitride glasses [1,2]. Silicon-oxycarbide refers specifically to a carbon-containing silicate glass wherein oxygen and carbon atoms share bonds with silicon in the amorphous network structure. Several amorphous silicon oxycarbide materials, prepared by sol-gel process, have been reported in the literature [3 - 5]. These materials can be efficiently obtained through the controlled pyrolysis process of polymeric gels derived from hydrolysis of methyl-substituted silicon alkoxides, for details see the review by Kroke et al. [6].

The cross-linking reaction of pre-ceramic polymers with or without catalyst and filler particles is one of the main processes involved in the polymer-to-ceramic conversion. During cross-linking, the inorganic network formation proceeds resulting in a significant change of the polymer rheology. The variation of elasticity and viscosity of the samples with time and temperature is of great importance for the final properties of the resulting ceramic material.

The present study is concerned with experimental rheological investigations related to the cross-linking process of polysiloxanes of the form $[CH_3\text{-}SiO_{3/2}]_x$. Moreover, a semi-empirical rheological model of the cross-linking process has been developed to model properly the evolution of the viscosity and elasticity of the preceramic polymer. The experiments have been performed with commercial MK polysiloxane (produced by Wacker, Germany) in presence of chemical catalyst (zirconium acetlyacetonate) and active filler ($MoSi_2$ powder produced by H.C. Starck, Germany).

2. Experimental

A commercial preceramic polymer, namely Wacker-Bensil PMS MK (MK polymer) obtained from Wacker Chemie GmbH, Burghausen (Germany), was used in our study. The MK polymer is a solid and solvent free silicone resin, poly(methylsilsesquioxane) of the form $[CH_3\text{-}SiO_{3/2}]_x$. The odorless, colorless flakes of MK-polymer has a softening range between 45-60 °C and a good solubility in organic solvents; namely, aromatic solvents and ketones. The polymer contains approximately 2 mol.% hydroxy and ethoxy groups, as functional units attached to silicon. Polycondensation at enhanced temperatures evolves water and ethanol which results in cross linking of the polymer and formation of a three dimensional Si-O-Si network. In order to achieve an acceptable process regime, a suitable thermal treatment in the presence of the catalyst zirconium acetylacetonate ($C_{20}H_{28}O_8Zr$) in the amount of 1 wt.% related to the polymer mass is used.

Rheological measurements were conducted by a controlled stress rheometer DSR 200 from Rheometrics using plate and plate configuration of 25 mm diameter and nominal gap of 0.6 mm. The polymer powder was mixed and homogenised with the catalyst and the active filler particles represented by $MoSi_2$ grains with the medium size of 2 μm. Subsequently the polymer mass was compacted in form of discs with 20 mm in diameter and 0.8 mm thickness. The test samples were placed on the lower plate of the rheometer, already heated up to the desired temperature. After the sample is completely melted, the rotational tool is fixed at the nominal gap and the upper heating system is got down to ensure an uniform temperature field all around the gap and the plates. Standard calibration of the rheometer and a complete test of the heating system were performed before starting the measurements.


a

3. Results and discussion

### 3.1 Experimental rheological investigation

The present experimental rheological investigation is based on the dynamic test at constant frequency and constant shear stress amplitude. The time evolution of elastic and viscous moduli, G' and G" respectively, are observed at $\omega = 1$ s^{-1}, as function of temperature and/or temperature gradient. The magnitude of the shear stress amplitude is maintained constant during each experiment at a value which limits the output level of strain amplitude at 0.1. From our previous investigation related to MK polymer, deformation processes that take place below a strain of 0.5 correspond to the linear viscoelastic regime of the samples. Following the increase of dynamic moduli with time, one can obtain valuable information on the development of the network strength and the temperature activation on the cross linking process, as a function of catalyst and filler concentration.

In Fig. 1 are represented the evolution of the rheological polymer properties with time at constant temperature in the presence of catalyst and as a function of the filler concentration. The temperature depending evolution of dynamic moduli for the same samples are shown in Fig. 2.

From Fig. 1 and Fig. 2. one can observe the direct relation between the active filler concentration and the increasing of reaction speed, respectively the increasing rate of dynamic moduli in time, respectively temperature, after the onset of cross-linking (defined as the minimum of G'). Same trend in the time evolution of G' is remarked in Fig. 3, where the influence of catalyst concentration is investigated.

b

c

d

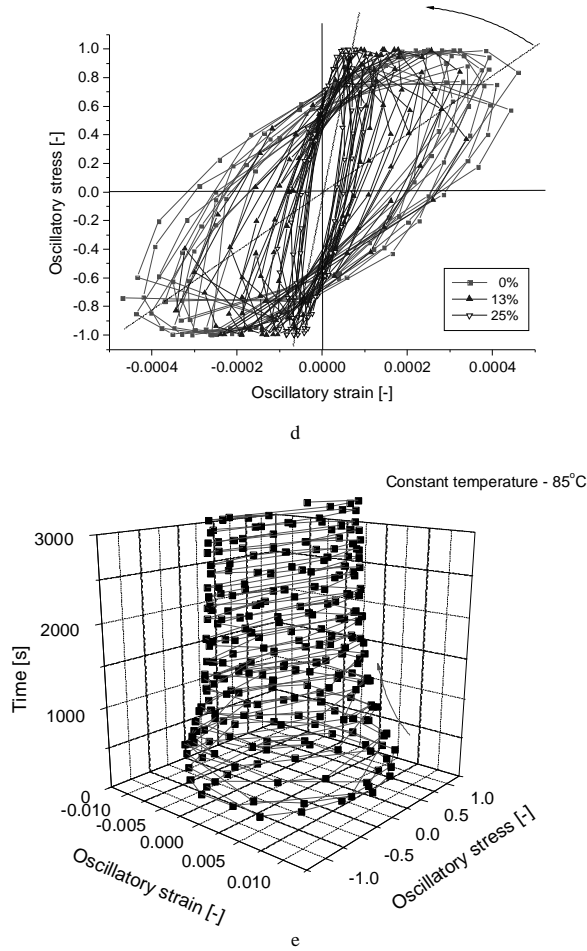Constant temperature - 85°C

e
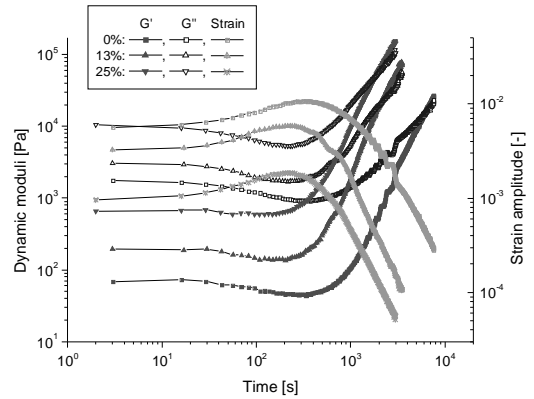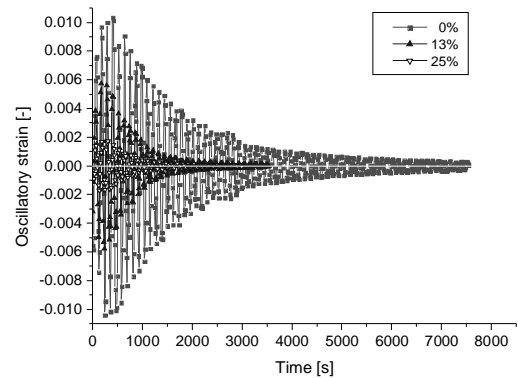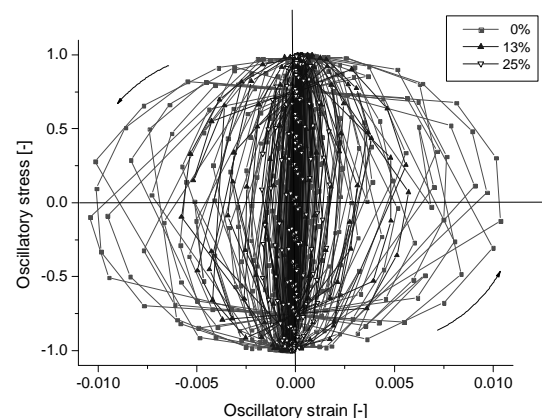
Fig. 1. Evolution of the rheological properties with time for the MK polymer + 1wt% catalyst, as function of the filler concentration, at constant temperature of 85 °C: a) Dynamic moduli and strain amplitude as function of time; b) Oscillatory strain as function of time; c) Time parametric Lissajous figures; d) Detailed time parametric Lissajous figures at small strains; e) 3D Lissajous figure in the absence of the filler.
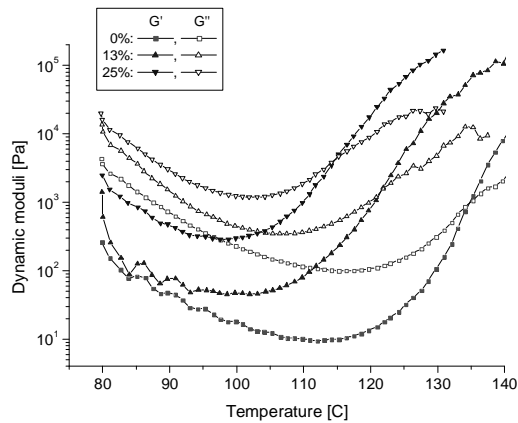

Fig. 2. Evolution of the dynamic moduli for MK + 1wt% catalyst, as function of temperature, for different filler concentrations (constant temperature ramp of 5 °C/min).
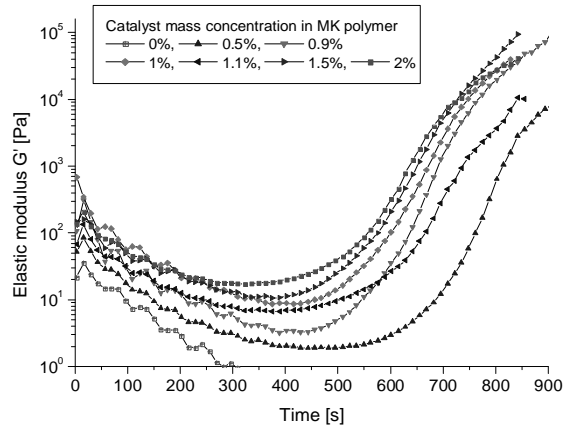

Fig. 3. Dependence of the elastic modulus with time for the MK polymer, as function of catalyst concentration, measured at a constant temperature ramp 5 °C/min.

In Fig. 4 is determined the influence of heating rate on the rheological properties of the MK polymer in the presence of catalyst. The experimentally founded 3D-Lissajous figure at a distinct heating rate is represented in Fig. 5.

A higher temperature ramp determine the onset of reaction earlier and at lower values of dynamic moduli (Fig. 4a), but at higher temperatures (Fig. 4b). It depends on each particular application how the heating history is correlated with the formulation of the sample.
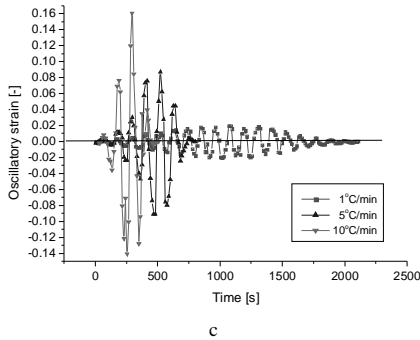

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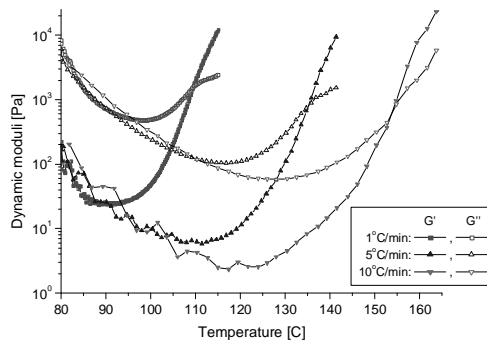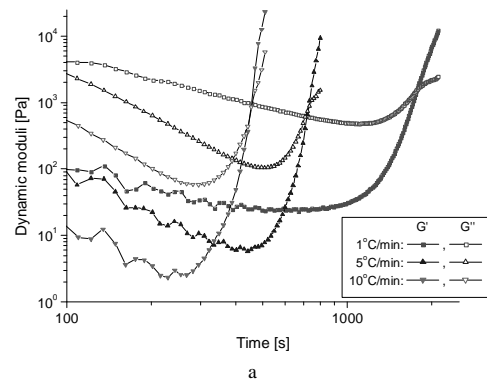
Fig. 4. Evolution of the rheological properties of the MK polymer + 1wt% catalyst, at 3 different temperature ramps: a) Dynamic moduli as function of time; b) Dynamic moduli as function of temperature; c) Oscillatory strain as function of time.

The dynamic test offers the opportunity to measure simultaneously viscosity (i.e. G'') and elasticity (i.e. G') during the reaction, both rheological properties being sensitive to the sample formulation, respectively percentage of catalyst and filler concentration. The time/temperature dependences of G' and G'' quantify the evolution of strength network, respectively the dynamics of cross-link reaction. Therefore, distinction between different formulations of the samples and heating procedures can be precise quantified from qualitative and quantitative points of view, see for example Fig. 1a and Fig. 4a The influence of filler concentration (Fig. 1 and Fig. 2) or catalyst concentration (Fig. 3) can be easily detected using the representation of experimental data against temperature, respectively time. The influence of heating history, respectively temperature ramp, on the reaction is put in evidence in Fig. 4. In some cases the parametric time evolution (Fig. 1c) or the 3D evolution (Fig. 1e and Fig. 5) of the oscillatory input- stress as function of oscillatory output-strain, i.e. the Lissajous figures, are very suggestive in representation of the cross-link process (for details see Balan and Riedel [7]).
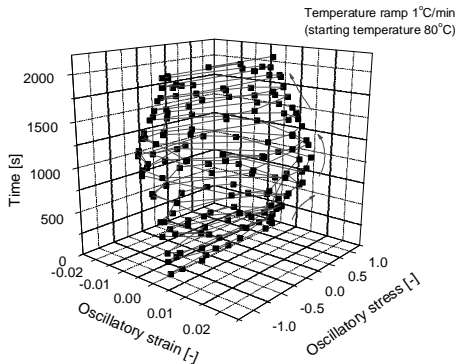

Fig. 5. 3D Lissajous figure at temperature ramp 1 ^{o}C/min for the MK polymer + 1wt% catalyst (see Fig. 4).

One concludes that rheology is an efficient procedure to evaluate the properties of polymer during the cross-linking reaction and to compare different samples as function of formulation and heating history. In the case of preceramic polymers the rheological investigations are able to characterise the process of polymer-to-ceramic conversion and to give at hand value information about the influence of filler concentration and heating rate on the transitory and final material properties.

3.2 Rheological model

The proposed model to describe the evolution of rheological properties of the samples during the cross-linking process is based on a constitutive relation of Jeffreys type, with dependence of the material functions on an internal parameter (i.e. the extent of reaction), which is assumed to be proportional to the reaction time (for details see reference [8] and also Fig. 6 that shows an analogous representation of the rheological model). The non-dimensional expression of the constitutive relation for simple shear flow, i.e. the dependence of the shear stress $\bar{\tau}$ on the strain γ and reaction time $\bar{t}$, is given by the equation (1):

$$\bar{\eta}_{S}(\bar{t})\dot{\bar{\tau}} + \overline{G}(\bar{t})\bar{\tau} = \left[\left(\bar{\eta}_{S}(\bar{t}) + \bar{\eta}_{G}(\bar{t})\right)\overline{G}(\bar{t}) + \bar{\eta}_{S}(\bar{t})\bar{\eta}_{G}(\bar{t})\right]\dot{\gamma} + \bar{\eta}_{S}(\bar{t})\bar{\eta}_{G}(\bar{t})\ddot{\gamma}$$
(1)

where $\quad \overline{G}=G/G^{*}, \quad \bar{\eta}_{S}=\eta_{S}/\eta^{*}, \quad \bar{\eta}_{G}=\eta_{G}/\eta^{*},$ $\bar{\tau}=\tau/G^{*}, \quad \bar{t}=t/t^{*}$ and the corresponding time derivatives (symbolized by the upper dot) are non-dimensional quantities (the characteristic physical quantities G^{*}, η^{*} and t^{*} are considered to be material and process dependent).
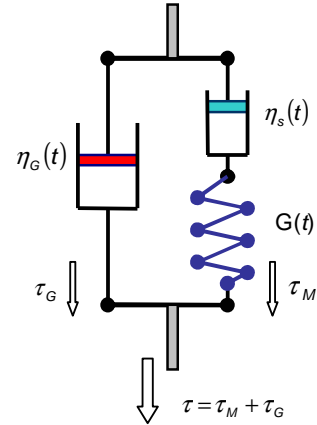

Fig. 6. Rheological model corresponding to the constitutive relation as shown in relation (1).

For the material functions in equation (1), namely the viscosities functions $\bar{\eta}_{S}$, $\bar{\eta}_{G}$ and the elastic modulus $\overline{G}$, the following expressions are proposed:

$$\bar{\eta}_{S}(\bar{t}) = \bar{\eta}_{0S}(0)\, e^{c_{1}\hat{t}^{m}} \cdot e^{-a_{1}\left(\frac{\theta-\theta_{0}}{\theta}\right)},$$
(2)

$$\bar{\eta}_{G}(\bar{t}) = \left[\bar{\eta}_{0G}(0) + \bar{\eta}_{\infty}\left(1 - e^{-c_{2}\hat{t}^{n}}\right)\right] \cdot e^{-a_{2}\left(\frac{\theta-\theta_{0}}{\theta}\right)},$$
(3)

$$\overline{G}(\bar{t}) = \left[\overline{G}_{0} + \overline{G}_{\infty}\left(1 - e^{-c_{3}\hat{t}'}\right)\right] \cdot e^{-a_{3}\left(\frac{\theta-\theta_{0}}{\theta}\right)}.$$
(4)

In relations (2), (3) and (4) $\overline{\eta}_{0S}(0)$, $\overline{\eta}_{0G}(0)$ and $\overline{G}_0$ represent the initial viscosities and initial elasticity of the elements at the reference temperature θ_0, respectively, $\overline{\eta}_\infty \gg \overline{\eta}_{0G}$ and $\overline{G}_\infty \gg \overline{G}_0$ are assumed characteristic values of the viscosity and elastic modulus for $\overline{t} \to \infty$.

The first expression in relations (2 – 4) model the cross linking process, i.e. the increasing of viscosity and elasticity of each element with the extend of reaction, respectively their evolution with the reaction time. Their second part is given by an exponential function which represents the dependence of materials property on the temperature θ at "a frozen point" of the reaction (in the form of Arrhenius law). Since the extend of reaction is directly temperature dependent, the cross linking process is also related to the temperature and is expressed by the dependence of the growing exponents (m, n and r) with temperature, according to equation (5):

$$m = m_0\left(\frac{\theta}{\theta_0}\right)^{em}, \; n = n_0\left(\frac{\theta}{\theta_0}\right)^{en}, \; r = r_0\left(\frac{\theta}{\theta_0}\right)^{er}. \quad (5)$$

The phenomenological constants c_1, c_2, c_3, a_1, a_2, a_3, respectively m_0, n_0, r_0 and em, en, er, are considered to be material dependent and have to be derived from experimental data. It is important to remark that at the end of reaction the proposed Jeffreys model (which defines a viscoelastic fluid behavior) becomes a Kelvin-Voigt model (i.e. a viscoelastic solid) due the asymptotic increase to infinity of the Maxwell's viscosity $\overline{\eta}_{0S}(\overline{t})$.

In the controlled stress oscillatory motion (i.e. the dynamic test performed in §3) on the material is applied a constant shear stress amplitude $\overline{\tau}_a$, with frequency $\overline{\omega}$; therefore, the input in (1) is given by relation (6):

$$\overline{\tau}(\overline{t}) = \overline{\tau}_a e^{i\overline{\omega}\overline{t}}. \quad (6)$$

The corresponding output is the oscillatory strain with strain amplitude $\gamma(\overline{t})$, which is assumed to have the form according to expression (7):

$$\gamma(\overline{t}) = \gamma_a(\overline{t}) e^{i(\overline{\omega}\overline{t} + \overline{\delta}(\overline{t}))} \quad (7)$$

(here $\overline{\delta}$ is the time dependent phase angle of the measured strain, see for details [9]).

The constitutive functions (2), (3) and (4) are introduced in equation (1), where the strain according to equation (7) is considered to be the unknown function for a given input (6). Finally, the solution $\gamma(\overline{t})$ is obtained using the specialized subroutine NDSolve of the commercial *Mathematica* code.

The present numerical simulations of equation (1) have been performed with the following numerical values: $\overline{\eta}_S(0) = \overline{\eta}_G(0) = 10$, $\overline{G}_0 = 10$; $\overline{G}_\infty = 10^5$, $\overline{\eta}_\infty = 10^3$; $c_1 = 0.5$, $c_2 = 0.02$, $c_3 = 0.001$; $m_0 = 4.5$, $n_0 = 0.5$, $r_0 = 2.5$. For simplicity, the material constants and the exponents in relations (2-5) were considered identical for all 3 material functions, respectively, $a_1 = a_2 = a_3 = 1$ and $em = en = er = 1.5$.

Some results of the simulations are represented in Fig. 7 for the isothermal process and in Fig. 8 are shows the results of model (1) at constant heating rate. In Fig. 9 is represented the influence of the magnitude of one growing exponent, respectively r_0, on the evolution of the process.
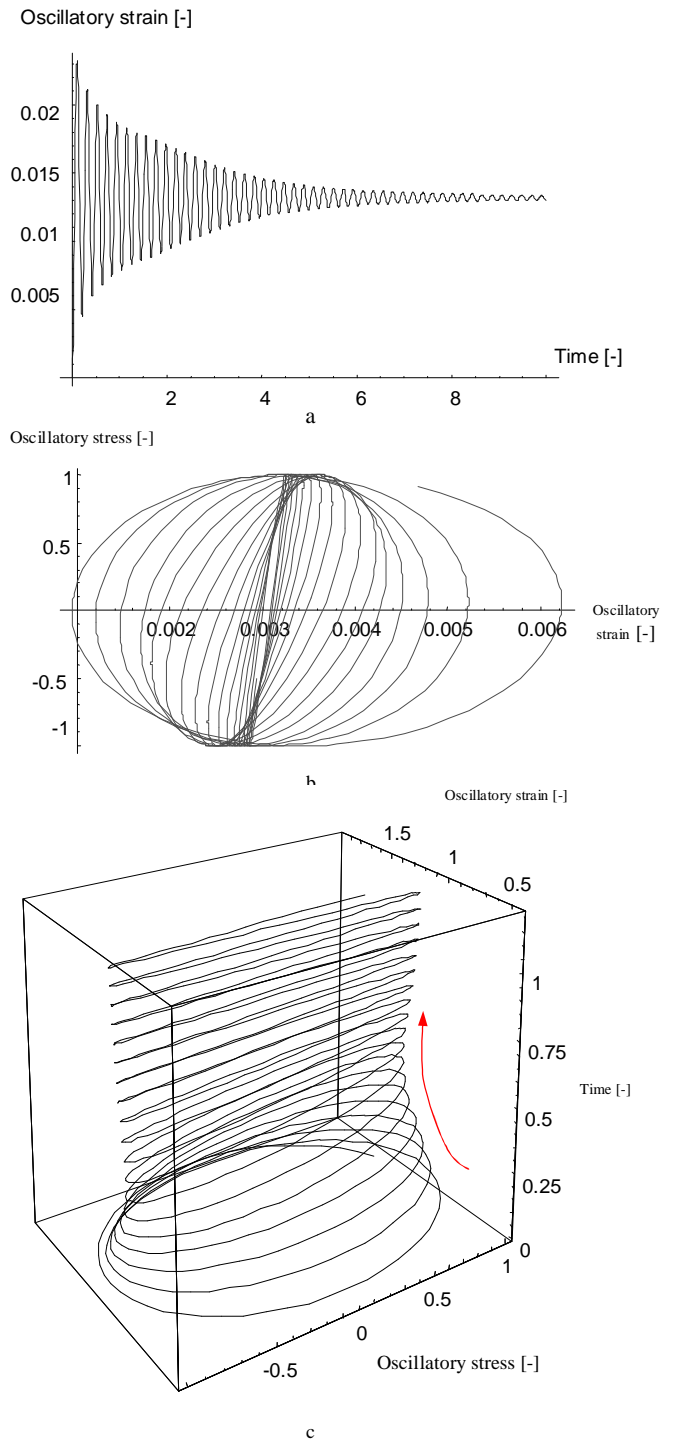

Fig. 7. Numerical simulation of model (1) in the dynamic test at constant shear stress amplitude, constant frequency and constant temperature: a) Oscillatory strain as function of non-dimensional time; b) Time parametric Lissajous figure; c) 3D Lissajous figure.

Comparison between experimental rheological data and present numerical simulations, as can be seen from Fig. 1b vs. Fig. 7a, Fig. 1c vs. Fig. 7b, Fig. 1e vs. Fig. 7c and Fig. 4c vs. Fig. 8a, proves that the proposed constitutive relation (1) is suitable to model properly the rheology of pre-ceramic polymers during the cross link process. The differential model (1) discloses the same qualitative evolution with time as that obtained experimentally both in isothermal and temperature dependent simulations. The simulation is sensitive to the change of the growing exponents, in particular to the change of filler or catalyst concentrations (which characterize the sample under investigation and, consequently, determine the values of material parameters – see Fig. 9 in comparison to the experiments from Fig. 1d). The non-dimensional relation (1) has a fundamental generality and flexibility in modeling the cross linking of pre-ceramic polymers. It takes into account the dependence of the materials function on the progress of the reaction, but has to be calibrated for each type of polymer sample, in order to fit the process also from a quantitative point of view.
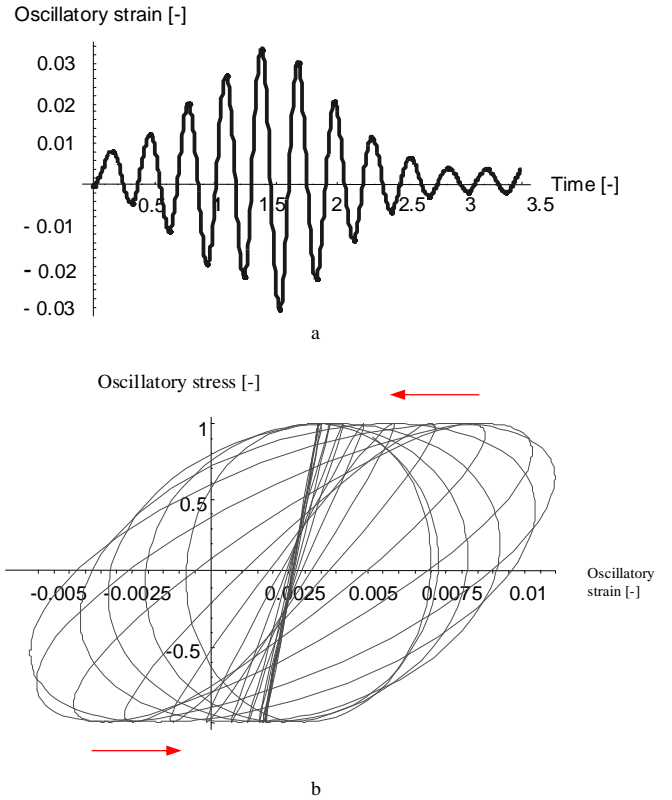

Fig. 8. Numerical simulation of model (1) in the dynamic test at constant shear stress amplitude, constant frequency and constant temperature ramp (heating rate – $\theta = \theta_0 + 50\,\bar{t}$ *): a) Oscillatory strain as function of non - dimensional time; b) Time parametric Lissajous figure.*
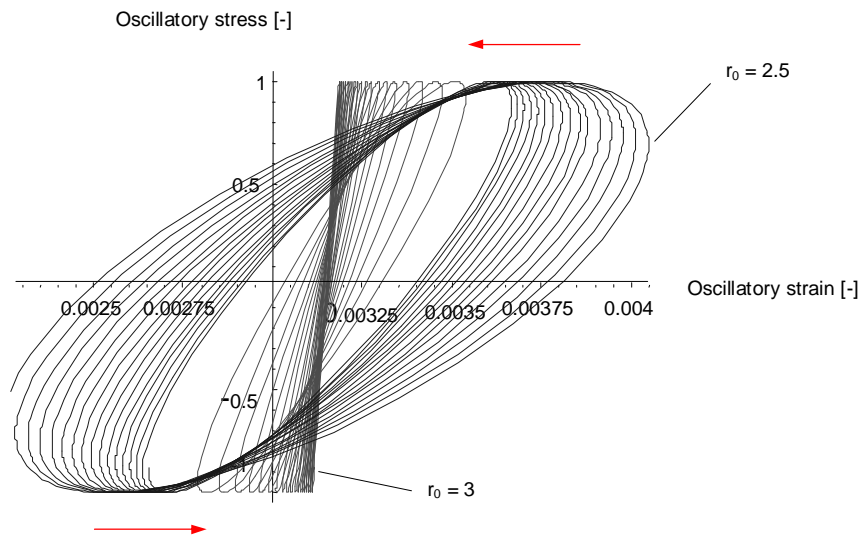

Fig. 9. Time parametric Lissajous figures, as function of the growing exponents; $r_0 = 2.5$ and $r_0 = 3$ (detail at small strains).

4. Conclusions

The work is dedicated to the rheological experimental investigation and modelling of the cross-linking reaction of pre-ceramic polymers in the presence of catalyst and/or fillers. The dynamic test at constant frequency is considered the most suitable experiment to observe simultaneously the evolution of viscosity and elasticity during the process, the most relevant flow properties with great influence of the final mechanical behaviour of the resulting ceramic material. In the formulation process of ceramic materials, the rheology of intermediate fluid phase of the samples is fundamental in establishing the percentage of additives and the corresponding heating rate. The great sensitivity of the proposed rheological test to the change in material formulation and temperature history is benefic for material scientists who design chemistry of ceramics for particular applications. The test procedure is relatively simple, can be easily implemented in laboratories and the experimental results have a direct impact on the design procedure of pre-ceramic polymers (similar experimental procedure has been proposed for different material, see [9]).

The experimental data are modelled with a novel constitutive relation which is able to reproduce the rheology of isothermal and non-isothermal cross-linking processes as a function of the reaction time. The constitutive relation is based on the 3-constants differential model, but the material parameters (2 viscosities and 1 elastic modulus) are here dependent on the reaction time and temperature. Each of the semi-empirical expression for that 3 material parameter contains 4 coefficients: 2 coefficients determine the growing of network and 2 coefficients characterise the temperature influence on the process. In total, the cross-linking reaction is modelled by 12 constants and the initial values for viscosities and elasticity at the reference temperature. Therefore, the model is flexible enough to fit properly almost any rheological behaviour during the cross-linking phenomena.

Qualitative agreement between experiments and numerical simulations of the process is obtained for all the investigated samples and tests heating histories. One can state as a final remark that the results of the present study indicate the value of rheological tests and rheological modelling to explore, to characterise and finally to determine the thermomechanical properties of pre-ceramic polymers.

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